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BENEFITS OF USING FGD GYPSUM FROM S.E. TURCENI IN AGRICULTURE

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Abstract. *From the perspective of environmental protection, the most important area of human activities is the industry. Industrial development has not taken into account that the progress of human society itself depends not only on the goods they offer, but also of the damage caused to the environment. In order for the environmental degradation from coal burning to be reduced we need to find solutions so the possibility of recovery of resulting sulphur oxides was considered. The gypsum resulting from the process of desulphurization has a very good quality, similar to natural gypsum. Therefore it can have many uses such as feedstock in the cement industry (3-5% of the cement composition); raw material in the building materials industry or in agriculture. This paper aims to analyze the potential benefits of applying FGD gypsum (flue gas desulphurization) to agricultural lands, benefits that can be chemical or physical.*

Key words: *flue gas desulphurization, gypsum, agricultural lands*

INTRODUCTION

Coal-fired electric power generating facilities employ a variety of combustion systems and flue gas treatment configurations. The exact configuration at a given plant depends on a wide range of factors including coal characteristics, availability of water, the type and amount of air pollutant control required, etc. Each piece of equipment used for power generation and/or air pollution control will affect the characteristics of the solid byproducts produced by that piece of equipment, and may affect the by-products of all other downstream components of the system. Devices whose primary purpose is flue gas desulfurization (FGD) can be located at various points within the combustion/flue gas treatment train.

The basic FGD process involves spraying an alkaline reagent into the combustion flue gas to react with SO_2 and water to form a precipitated salt by-product. The by-product can be filtered from the system and either disposed in landfills or recycled for beneficial use. Lime or limestone is typically used as the reagent; although sodium-based reagents can also be used for FGD. Depending on the type of FGD process, the predominant by-product is calcium sulfite, hydrated calcium sulfate (gypsum), non-hydrated calcium sulfate (anhydrite), or some mixture of the three salts. Unused alkaline reagent in varying amounts can also be carried through to the by-product stream. The FGD process can be further classified as either wet or dry, depending on the amount of water used to spray the reagent into the flue gas.

MATERIAL AND METHODS

Analyzing the methods of retaining SO_2 from flue gases used worldwide and considering the provisions of environmental legislation, it was decided that the energetic blocks from S.C. Turceni Energy Complex S.A. to be equipped with limestone - gypsum wet-type desulphurization installations.

In this process, SO_2 reacts with the absorbing agent (limestone) from the reaction resulting in a new product (gypsum).

They are especially preferred at facilities that burn highsulfur coals where high-efficiency SO_2 removal is required. The capital cost of wet FGD systems is quite high, but SO_2 removal efficiencies are typically greater than 95%. Figure 1 illustrates a typical wet FGD system consisting of a set of “absorber” vessels located downstream of the primary particulate removal device, usually an electrostatic precipitator (ESP) or fabric filter (baghouse). In such a configuration, the FGD by-product comprises only the salts formed by the FGD reaction, along with some reagent carryover and water.

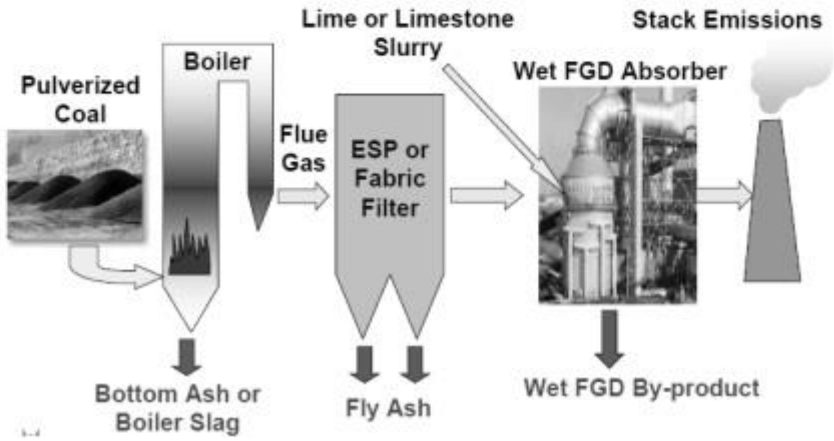

Figure 1. Typical wet FGD system

The flue gases from burning lignite in the boiler will be treated in an absorber tower by being washed countercurrent with a limestone solution with a mass concentration of 30%.

Flue gas flow needed to be treated - for boilers of 1035 t/h from SC CE Turceni SA – is of 1.723 million Nm^3/h dry at 6% O_2. SO_2 content (6% O_2, dry) was 5.600 mg/Nm^3 dry at 6% O_2 and the dust content was max 100mg / Nm^3.

Formation of FGD Gypsum (Solution Chemistry)

• Dissolution of SO_2

$$SO_2 + H_2O \rightarrow 2H+ + SO_3^{2-}$$

• Hydration of Lime

$$CaO + H_2O \rightarrow Ca(OH)_2$$

• Dissolution of Hydrated Lime

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^{1-}$$

• Reaction of SO_2 with Ca^{2+}

$$Ca^{2+} + SO_3^{2-} + 2H_2O \rightarrow CaSO_3.1/2H_2O + 3/2\ H_2O$$

• Acidification of the material

$$CaSO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2SO_3$$

• Formation of calcium bisulfite

$$CaSO_3 + H_2SO_3 \rightarrow Ca(HSO_3)_2$$

• Oxidation of calcium bisulfite to gypsum

$$Ca(HSO_3)_2 + H_2O + ½\ O_2 \rightarrow CaSO_4.\ 2\ H_2O + SO_2$$

Limestone Forced Oxidation Flue-Gas Desulfurization Process

$$SO_2 + CaCO_3 \rightarrow CaSO_3 \cdot ½H_2O + CO_2 + O_2 \rightarrow CaSO_4 \cdot 2H_2O \text{ (gypsum)}$$

On formation of a precipitate from solution, dissolved constituents must partition between the solid and liquid phases.

The type of salt formed by the SO_2 conversion reaction depends on the degree of oxidation introduced into the FGD system. Gypsum ($CaSO_4 \cdot 2H_2O$) is formed when oxidation is enhanced, while calcium sulfite ($CaSO_3 \cdot ½\ H_2O$) is the dominant salt when oxidation is inhibited (Figure 2). Oxidation to produce FGD gypsum can be achieved either by introducing excess air into the absorber vessel or employing an external oxidation tank.

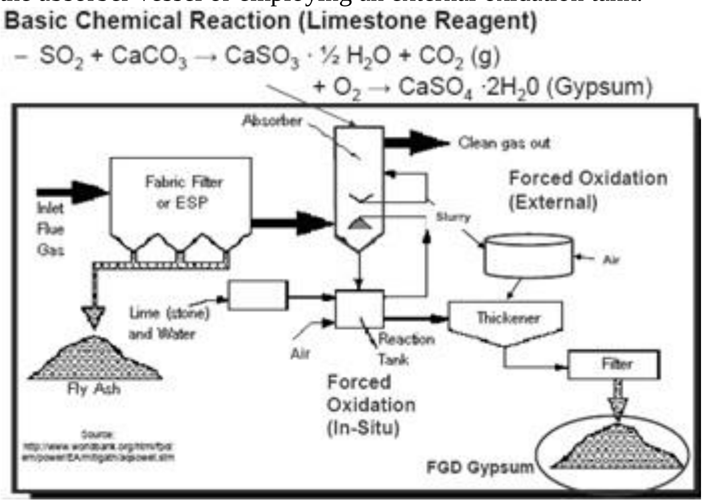

Figure 2. FGD Gypsum formation

FGD gypsum is used most commonly as a raw material for the manufacture of wallboard, and it can also be readily re-used as an agricultural supplement or in the manufacture of cement.

RESULTS AND DISCUSSIONS

Resulting FGD gypsum characteristics are:
- Purity ($CaSO_4\ 2H_2O$)> 95% (dry basis)
- Moisture content <10 wt%
- Cl <0.01wt%
- Particle size> 35 μm
- PH value from 6 to 8

The quality of the FGD gypsum resulting from the process of desulfurization is very good, similar to natural gypsum.

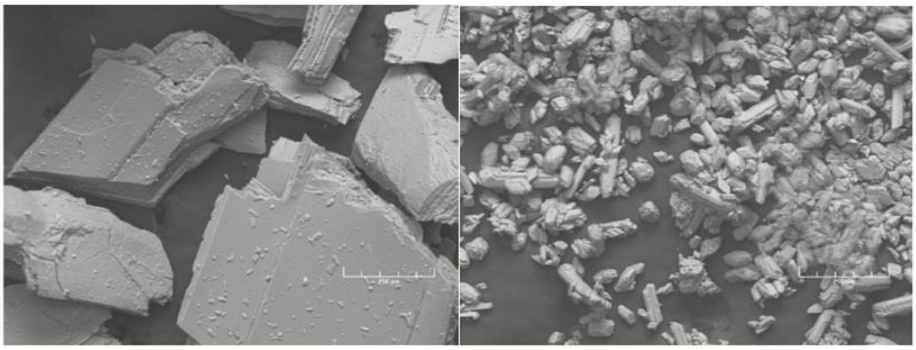

Figure 3. Comparison Between natural gypsum (left) and FGD gypsum (right)
Natural gypsum crystals shown here are small fractions of larger flat and blocky crystals. FGD Gypsum has smaller crystals, which tend to be elongated, few being larger than 200μm.

Here are highlighted five key (and overlapping) benefits of FGD Gypsum:

1. Source of calcium and sulfur for plant nutrition.

Plants require relatively large amounts of Ca and S, Ca – 0.5% shoot dry weight and S – 0.1% to 0.5% dry weight for optimal growth. FGD Gypsum supplies Ca and S for plant nutrition.

The predominant proportion of the organic sulfur is present in the protein fraction (up to 70% of total sulfur), as cysteine and methionine (two amino acids) residues.

Cysteine and methionine are highly significant in the structure, conformation and function of proteins. Plants contain a large variety of other organic sulfur compounds, as thiols (glutathione), sulfolipids and secondary sulfur compounds (alliins, glucosinolates, phytochelatins), which play an important role in physiology and protection against environmental stress and pests.

Calcium in plants is required for proper functioning of cell membranes and cell walls, needed in large amounts at tips of growing roots and shoots and in developing fruits. Relatively little Ca is transported in phloem. Ca needed by shoot tips is transported in the transpiration stream of xylem and Ca needed by root tips comes from soil solution

Ca supplied by FGD Gypsum prevents: blossom end rot of watermelons and tomatoes and bitter pit in apples.

For crops FGD Gypsum gives balanced nutrients, moisture and oxygen, makes the soil more usable. The plants have greater root volume into the subsoil, reduced stress season–long, greater vigor during extreme weather events and at some crops there was observed an increased crop production efficiency. (figure 4)

Figure 4. Increased crop production efficiency

2. Improves acid soils and treats aluminum toxicity. One of FGD Gypsum's main advantages is its ability to reduce aluminum toxicity, which often accompanies soil acidity, particularly in subsoils. FGD Gypsum can improve some acid soils even beyond what lime can do for them, which makes it possible to have deeper rooting with resulting benefits to the crops.

Figure 5. Higher quality rooting environment

3. Improves soil structure. Flocculation, or aggregation, is needed to give favorable soil structure for root growth and air and water movement

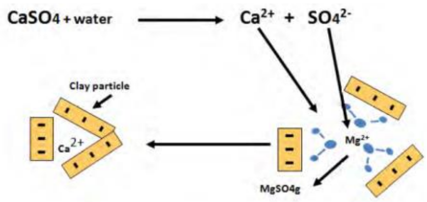

Figure 6. Gypsum flocculating clay particles

Figure 7. Influence of FGD gypsum applied at different rates, on the dispersion and flocculation of a soil

In some situations FGD gypsum may be useful to improve soil properties to enhance biomass production while protecting environmental quality

4. Improves water infiltration. FGD Gypsum also improves the ability of soil to drain and not become waterlogged due to a combination of high sodium, swelling clay and excess water. Increased water-use efficiency of crops is extremely important during a drought. Better soil structure allows all the positive benefits of soil-water relations to occur and FGD Gypsum helps to create and support good soil structure properties.

Figure 8. Permeability of the soil increased with gypsum

5. Helps reduce runoff and erosion. Agriculture is considered to be one of the major contributors to water quality, with phosphorus runoff the biggest concern.

Using FGD Gypsum as a soil amendment is the most economical way to cut the non-point run-off pollution of phosphorus.

CONCLUSIONS

There are a number of potential benefits of applying FGD gypsum to agricultural soils. These can be either chemical or physical.

Chemical benefits result from supplying essential plant nutrients calcium (Ca) and sulfur (S) for crop production or by modifying the subsoil to create a more favorable medium for plant root development (e.g., decreasing aluminum (Al) toxicity, promoting clay flocculation, enhancing root penetration, increasing water extraction from subsoil layers, etc.).

The physical benefits include the promotion of clay flocculation and aggregation of the soil, reduction of surface crusting which leads to increased water infiltration. These changes result in reduced runoff and erosion. For example, application of FGD material improves soil chemistry and increases water availability and crop yield as a result of reduction of subsoil chemical restrictions on rooting depth, while at the same time increasing water infiltration into the surface soil. A number of soil physical and related properties have been positively affected by the use of FGD gypsum such as reduced strength of subsoil hardpan layers. Improved soil aggregation leads to improved soil aeration and reduced bulk density.

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